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Electrochemical treatment of actual dye house effluents using electrocoagulation process directly powered by photovoltaic energy

D. Marmanis[a], K. Dermentzis[a,b,*], A. Christoforidis[a,b], K. Ouzounis[c], A. Moumtzakis[c]

[a]*Department of Petroleum & Natural Gas Technology, Eastern Macedonia and Thrace Institute of Technology, 65404 Agios Loucas, Kavala, Greece, Tel. +30251046229; email: marmanis@teikav.edu.gr (D. Marmanis), Tel. +302510462247, +302510245133; email: demerz@otenet.gr (K. Dermentzis), Tel. +30251046229, +302510462247; email: achrist@teikav.edu.gr (A. Christoforidis)*
[b]*Hephaestus Research Center, Eastern Macedonia and Thrace Institute of Technology, 65404 Agios Loucas, Kavala, Greece*
[c]*Department of Environmental Engineering, Democritus University of Thrace, 67100 Xanthi, Greece, Tel. +302541079886; emails: ouzounis@env.duth.gr (K. Ouzounis), amoumtza@env.duth.gr (A. Moumtzakis)*

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ABSTRACT

In the present work, the decolorization treatment of colored wastewaters produced from polyamide textile dyeing is studied using the electrocoagulation process with sacrificial aluminum electrodes. The electrical energy is obtained from a solar photovoltaic array by directly connecting it to the electrocoagulator without batteries. The photovoltaic electrocoagulation (PV-EC) system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current intensity supplied by the photovoltaic array. All the PV-EC experiments were performed in Kavala Institute of Technology (latitude 40˚55′, longitude 24˚22′, and altitude 138 m above the sea level). The purpose of this paper is to investigate all parameters affecting the efficiency of the process, such as initial wastewater pH, conductivity, operating time, flow rate, and solar irradiation. The efficiency of the EC process was followed by measurements of turbidity and chemical oxygen demand (COD). According to the obtained experimental results, fast and effective decolorization of the treated wastewater occurred in a few minutes of electroprocessing. Turbidity was quantitatively reduced from 103 to 0.2 NTU, amounting to a removal percentage of over 99%, whereas COD was reduced by 65%. The proposed process is appropriate for decolorizing colored textile dye wastewaters and especially for small applications in remote and isolated locations without connection to public electric grid.

Keywords: Dye house effluents; Decolorization; Electrochemical coagulation; Photovoltaic solar energy

1. Introduction

The textile industry consumes enormous amounts of water during dyeing and finishing operations. Typical medium-scale textile factories produce approximately 1,000 m^3 of colored wastewater per day. Dye-bearing wastewaters are toxic for the environment, since dyes are stable chemical compounds with low biodegradability. The discharge of colored and toxic wastewater into the ecosystem causes chemical as well as biological changes, and remains a problem.

*Corresponding author.

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Dye house industries are under pressure to reduce the color in effluents and search for "greener" methods that are more effective and less polluting. For these reasons, it is necessary to treat textile effluents prior to their discharge into the receiving water.

Several biological, physical, and chemical treatment processes have been suggested for the removal of dyes from aqueous waste streams, such as adsorption, biosorption, membrane processes, advanced oxidation, chemical coagulation, flocculation, and electrochemical methods such as electrooxidation [1–3] and electrocoagulation [4–11].

Conventional biological processes are often less successful, because most of dyes are barely or nonbiodegradable [12]. Electrochemical processes have been proved viable alternatives or complementary to biological treatment in some instances, especially when pollutants are recalcitrant to biological processing.

Electrocoagulation (EC) is an emerging technique for water remediation closely related to chemical coagulation, which has been used in the last decades for wastewater remediation. This process consists of providing electrical current to a sacrificial anode and creating metallic hydroxide flocs inside the wastewater by electrodissolution of soluble anodes made of aluminum or iron.

The main reactions occurring during electrocoagulation with aluminum electrodes produce aluminum ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

$$2H_2O + 2e- \rightarrow 2OH^{-} + H_2 \quad (2)$$

The generated Al^{3+} and OH^{-} ions react to form various monomeric and polymeric species such as $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{7+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$, which finally result in *in situ* formation of gelatinous $Al(OH)_3$ effecting the coagulation and co-precipitation of particulates from the solution by adsorption [5].

The gas bubbles produced during electrolysis support the flotation of the floccules and carry the pollutants to the top of the solution, where they are concentrated, collected, and removed. The created sludge is separated by filtration. The removal mechanisms in EC may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation, and flotation.

Environmental pollution has taken dangerous proportions. Therefore, nowadays the need for the development of renewable and more environmental-friendly energy sources is in great demand. In recent years, the photovoltaic (PV) solar energy has become one of the most popular renewable energy sources, which, as autonomous, is very helpful for small applications especially in remote and isolated locations with lack of electric grid [13–17]. The PV power is abundant with long life and low cost for maintenance. Furthermore, PV modules produce direct current which can directly be used for the electrochemical processes. It implies that the treatment of wastewaters depends on solar radiation, which depends on geographical location, meteorological conditions, season, time of day, and PV array configuration.

The present paper discusses an electrochemical decolorization/degradation treatment of actual dye house effluent using the electrocoagulation process with aluminum electrodes, which is directly powered by a PV array. The photovoltaic electrocoagulation (PV-EC) system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current density supplied by the PV array. Operating parameters that affect the PV-EC process, such as pH, current density, conductivity, flow rate, operating time, and solar irradiation are determined.

2. Methods

The textile dyeing wastewater was obtained from a factory located near Xanthi in northern Greece. The main characteristics of the wastewater are shown in Table 1.

The photovoltaic module used was SUNPOWER (Maxeon Cell Technology) SPR-327NE-WHT-D made from monocrystalline silicon with a surface area of 1.63 m^2 and a peak power of 327 W. The experiments were conducted in Kavala Institute of Technology (latitude 40°55′, longitude 24°22′, and altitude 138 m above the sea level).

Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (WTW). The pH and the

Table 1
Typical characteristics of used actual dye house effluents

Parameters	Value
Initial pH	6.5
COD (mg/L)	1,836
Turbidity (NTU)	103
Conductivity (μS/cm)	700
Temperature (°C)	22

temperature were determined by a pH-meter (WTW). The wastewater was circulated by a peristaltic pump.

The wastewater was first filtered with a screen filter to remove large suspended solids before being used for the experiments. All electrocoagulation experiments were conducted at room temperature in a 500 mL electrochemical reactor in which aliquot solutions of 200 mL were placed and slowly stirred with a magnetic bar at 500 rpm. Three commercially obtained aluminum plates installed vertically in the reactor with the dimensions $10 \times 3.5 \times 0.5$ cm, immersed to a 7 cm depth with an effective area of 49 cm^2 each, were used as electrodes in the experiments. The electrodes were situated 0.5 cm apart from each other. To remove the oxide and passivation layer from aluminum surface, the electrodes were grinded with sandpaper and activated by dipping them in 5 N HCl solution for 1 min. KCl was added to every treated solution. The added KCl serves for the prevention of passivation on the aluminum electrode surface and decrease of the excessive ohmic resistance in the solution. The polarity of the cell was reversed every 30 min to limit the formation of passivation layers on the electrodes. Samples were extracted every 10 min and filtered with Whatman filter paper (Grade 40) and then analyzed. At the end of each experiment, the produced sludge and the mass loss of the aluminum electrodes were measured. Chemical oxygen demand (COD) reactor (Thermoreaktor TR 420, MERCK) was used for the determination of COD. The turbidity (NTU) of samples was analyzed by a Turbidimeter (AQUALYTIC AL-100).

Fig. 1 shows the experimental setup.

3. Results and discussion

3.1. Effect of operating parameters

Several operating parameters such as initial pH, current density, conductivity, flow rate, contact time, and electrode type can influence the removal efficiencies of COD and turbidity in the PV-EC process. In the present paper, all these parameters are investigated in order to evaluate a treatment technology for decolorization of colored wastewaters from actual dye house effluents. The experiments described in Sections 3.1.1–3.1.3 are conducted batch wise, while those described in Section 3.1.4 are conducted in a continuous mode of operation.

3.1.1. Effect of initial pH

During the treatment of dye house effluents by electrocoagulation, the pH value of wastewater changes, due to the evolution of $H_{2(g)}$ and the generation of OH^- ions at the cathode. The electrocoagulation process is affected by the initial wastewater pH. Experiments were conducted at the constant current density of 15 mA/cm^2, constant operation time of 40 min, and various initial pH values of 2.5, 4, 5.6, 7, and 8.5 (Table 2). It was found that maximum COD and turbidity removal occur in the slightly acidic pH range 4–7 with optimum pH = 5.6 (Table 2). The reduction in the removal efficiency in strong acidic and also strong alkaline pH is also described by other researchers [4–6].

At pH < 4, the removal percent of pollutants is low. It increases considerably at pH 4, remains high in

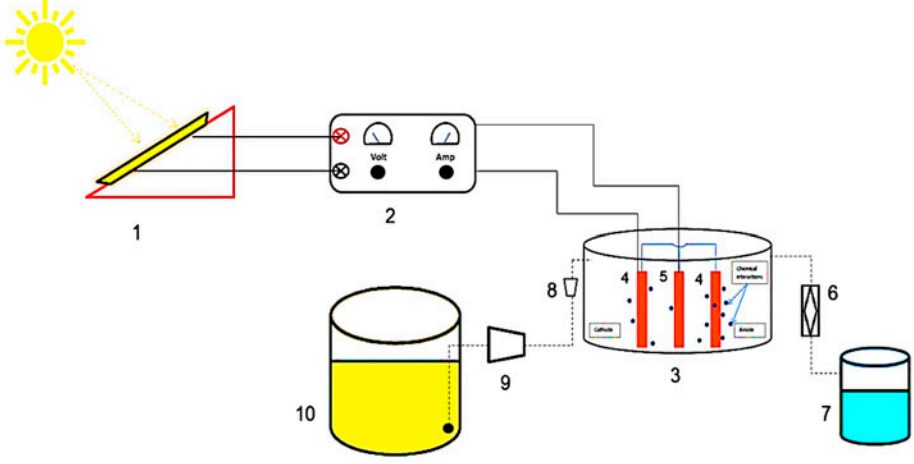

Fig. 1. Diagram of the experimental setup. 1. PV Solar module, 2. Regulator, 3. Electrocoagulation reactor, 4. Electrode (a), 5. Electrode (b), 6. Filter, 7. Treated solution, 8. Flow meter, 9. Peristaltic pump, and 10. Wastewater deposit.

Table 2
COD and turbidity removal percentage at various initial wastewater pH values

	pH = 2	pH = 4	pH = 5.6	pH = 7	pH = 8.5
COD removal (%)	22.1	53.7	64.8	57.6	50.4
Turbidity removal (%)	65.5	92.4	99.8	93.5	91.7

Table 3
COD and turbidity variation with operation time

Time (min)	COD (mg/L)	COD removal (%)	Turbidity (NTU)	Turbidity removal (%)	pH
0	1,836		103		5.6
10	1,130	38.45	0.4	99.61	6.2
20	734	60.02	0.2	99.8	6.5
30	680	62.96			6.8
40	646	64.81			7.2

the pH range 4–7, and decreases at pH > 7. In alkaline medium (pH > 8), the final pH does not change significantly because the electrochemically generated OH^- ions at the cathode are consumed by the electrochemically generated Al^{3+} ions at the anode forming the needed $Al(OH)_3$ flocs.

3.1.2. Effect of operating time

It is known that during the EC process, the increased operating time increases the coagulant and the bubble production rate, flocs size, and growth leading to increased removal of pollutants.

Measurements are carried out at the constant current density of 15 mA/cm^2, constant conductivity of 1,600 μS/cm, and initial pH of 5.6 using Al electrodes. According to Table 3, the removal rate of COD increases, as expected, with increasing operating time. When all other factors are held constant the removal efficiencies of COD at 10, 20, 30, and 40 min of electrolysis time are 38.45, 60.02, 62.96, and 64.81%, respectively. As can be seen in Table 3, the initial turbidity decreased from 103 NTU to 0.4 and 0.2 NTU after 10 and 20 min of electrolysis time, respectively. With increasing running time of the experiment, higher COD and turbidity removal efficiencies were obtained because more aluminum ions are generated by dissolution of the anode, which act as the coagulant. Also, the produced hydrogen gas bubbles contribute to an additional removal of pollutants by electroflotation.

As shown in Table 2, after the EC treatment, COD can be reduced to about 65%. Higher COD removal (>90%) can be achieved by advanced electrochemical oxidation using boron-doped diamond electrodes at the elevated temperature of 60°C.

3.1.3. Effect of conductivity

The wastewater conductivity affects immediately the applied voltage and, therefore, the electrical energy consumption. The removal percentage of COD and turbidity in the textile dyeing wastewater is hardly affected and remains constant over 64 and 99%, respectively, for all three tested wastewater conductivities of 800, 1,600, and 3,200 μS/cm (Table 4). The initial wastewater conductivity of 700 μS/cm was adjusted to 800, 1,600, and 3,200 μS/cm by the addition of KCl electrolyte.

3.1.4. Effect of flow rate

The current density supplied by the PV array depends on the solar irradiation and the temperature

Table 4
Electrocoagulation results for different wastewater conductivities

Conductivity (μS/cm)	Voltage (V)	Energy consumption (kWh/m^3)	COD removal (%)	Turbidity removal (%)
800	33.3	81.3	64.5	99.5
1,600	16.6	39.8	64.8	99.8
3,200	7.9	16.1	64.7	99.6

Table 5
EC results for different wastewater flow rates

Flow rate (L/h)	Current density (mA/cm^2)	Voltage (V)	Residence time (min)	Turbidity removal (%)	COD removal (%)
1.0	15	8.7	12	99.8	64.8
2.0	30	16.3	6	99.6	64.6
3.0	45	24.2	4	99.3	64.2

Table 6
Experimental conditions and measured parameters for different meteorological conditions

Month	Ideal tilt azimuth = 1,800	Solar radiation sunny day kWh/m^2	Solar radiation cloudy day kWh/m^2	Solar radiation sunny day kW/m^2	Solar radiation cloudy day kW/m^2
January	52	3.02	2.15	0.378	0.268
February	43	3.63	2.60	0.404	0.289
March	31	4.61	3.34	0.512	0.371
April	18	5.53	4.15	0.582	0.437
May	6	6.27	4.83	0.660	0.508
June	0	6.68	5.35	0.703	0.563
July	2	6.43	5.24	0.677	0.551
August	14	5.84	4.79	0.615	0.504
September	30	5.09	4.15	0.566	0.461
October	45	4.34	3.51	0.482	0.390
November	56	3.64	2.80	0.455	0.350
December	57	3.07	2.24	0.409	0.299
Totals yearly avg		58.15	45.13	0.537	0.416

of the PV modules. These parameters cannot be controlled and will change continuously through the hours in a day or suddenly through clouds crossing or changes in wind speed. Valero et al. and Ortiz et al. [16,17] proposed a clever mode of operation in order to make the PV-EC system versatile to instantaneous solar irradiation by keeping constant the ratio current density/flow rate. Thus, when the current density supplied by the PV array changes, also the working flow rate must proportionally change to maintain this ratio constant. This way of operation implies that the volume of treated wastewater is directly related to the solar energy incident on the panels.

The experiments with constant current density and flow rate were conducted at a sunny midday and in short periods to keep approximately constant values of solar irradiation. As can be obtained from Table 5, by increasing the current density, the cell voltage and the flow rate increase proportionally, while the residence time decreases. The removal percentage of turbidity and COD is not affected and remains near 99 and 65%, respectively.

3.2. Solar irradiation for different meteorological conditions

In an electrocoagulation process, powered directly by photovoltaic solar modules, the current intensity supplied by the panels changes according to solar irradiation. The solar irradiation intensity depends on the occasional meteorological/geographical conditions and influences the photovoltaic output current and, therefore, the efficiency of pollutants removal. As stated in Section 3.1.4, the flow rate of the treated wastewater can be used as the control parameter.

The measured parameters for different meteorological conditions are tabulated in Table 6. This table contains the actual solar radiation (kWh/m) for sunny and cloudy days, respectively, throughout the year. As is seen in Table 6, the solar radiation changes during the year in a continuous way (i.e. though the months in a year) or suddenly (i.e. sunny or cloudy day).

4. Conclusions

This paper shows the feasibility of performing remediation of dye house effluents by directly

connecting the electrocoagulation reactor to the photovoltaic generator. The current density supplied by the PV array depends on the solar irradiation and the temperature of the photovoltaic modules. However, the PV-EC system is made versatile to instantaneous solar irradiation by adjusting the flow rate of the treated wastewater and keeping constant the ratio current density/flow rate. The removal percentage of turbidity and COD remains high for the three tested wastewater flow rates of 1.0, 2.0, and 3.0 L/h, and the three wastewater conductivities of 800, 1,600, and 3,200 μS/cm. Based on the experimental results, it can be concluded that the proposed PV-EC process could present some advantages for wastewater purification applications in isolated places without connection to public electric grid.

References

[1] E. Chatzisymeon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Electrochemical treatment of textile dyes and dyehouse effluents, J. Hazard. Mater. B137 (2006) 998–1007.
[2] K. Dermentzis, D. Marmanis, E. Valsamidou, A. Christoforidis, K. Ouzounis, Electrochemical decolorization treatment of nickel phthalocyanine reactive dye wastewater, Environ. Eng. Manage. J. 10 (2011) 1703–1709.
[3] P. Kumar, T.T. Teng, S. Chand, K.L. Wasewar, Fenton oxidation of carpet dyeing wastewater for removal of COD and color, Desalin. Water Treat. 28 (2011) 260–264.
[4] I. Kabdaşlı, T. Arslan, I. Arslan-Alaton, T. Ölmez-Hancı, O. Tünay, Organic matter and heavy metal removals from complexed metal plating effluent by the combined electrocoagulation/Fenton process, Water Sci. Technol. 61 (2010) 2617–2624.
[5] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminium electrodes, J. Hazard. Mater. B100 (2003) 163–178.
[6] V. Khandegar, A.K. Saroha, Electrocoagulation for the treatment of textile industry effluent—A review, J. Environ. Manage. 128C (2013) 949–963.
[7] N. Drouiche, H. Lounici, M. Drouiche, N. Mameri, N. Ghaffour, Removal of fluoride from photovoltaic wastewater by electrocoagulation and products characteristics, Desalin. Water Treat. 7 (2009) 236–241.
[8] N. Drouiche, S. Aoudj, H. Lounici, H. Mahmoudi, N. Ghaffour, M.F.A. Goosen, Development of an empirical model for fluoride removal from photovoltaic wastewater by electrocoagulation process, Desalin. Water Treat. 29 (2011) 96–102.
[9] H. Moreno, J.R. Parga, J.A. Gomes, M. Rodríguez, Electrocoagulation treatment of municipal wastewater in Torreon Mexico, Desalin. Water Treat. 51 (2013) 2710–2717.
[10] W. Lemlikchi, S. Khaldi, M.O. Mecherri, H. Lounici, N. Drouiche, Degradation of Disperse Red 167 Azo Dye by bipolar electrocoagulation, Sep. Sci. Technol. 47 (2012) 1682–1688.
[11] D-G. Kim, R.J.S. Palacios, S.O. Ko, Characterization of sludge generated by electrocoagulation for the removal of heavy metals, Desalin. Water Treat. 52 (2014) 909–919.
[12] M.I. Beydill, R.D. Matthews, S.G. Pavlostathis, Decolorization of a reactive copper-phthalocyanine dye under methanogenic conditions, Water Sci. Technol. 43 (2001) 333–340.
[13] A.A. Irfan, Photovoltaic Application in Remote Areas, Asian Institute of Technology, Bangkok, 1997.
[14] E. Alvarez-Guerra, A. Dominguez-Ramos, A. Irabien, Design of the photovoltaic solar electro-oxidation (PSEO) process for wastewater treatment, Chem. Eng. Res. Des. 89 (2011) 2679–2685.
[15] S. Zhang, J. Zhang, W. Wang, F. Li, X. Cheng, Removal of phosphate from landscape water using an electrocoagulation process powered directly by photovoltaic solar modules, Sol. Energy Mater. Sol. Cells 117 (2013) 73–80.
[16] D. Valero, J.M. Ortiz, E. Exposito, V. Montiel, A. Aldaz, Electrocoagulation of a synthetic textile effluent powered by photovoltaic energy without batteries: Direct connection behaviour, Sol. Energy Mater. Sol. Cells 92 (2008) 291–297.
[17] J.M. Ortiz, E. Expósito, F. Gallud, V. García-García, V. Montiel, A. Aldaz, Electrodialysis of brackish water powered by photovoltaic energy without batteries: Direct connection behaviour, Desalination 208 (2007) 89–100.